SCIENCE FOR CERAMIC PRODUCTION

X-RAY PHOTOELECTRON SPECTROSCOPY OF A COMPLICATED CERAMIC OXIDE OF THE SYSTEM BeO – TiO$_2$ – C

M. V. Kuznetsov,[1] V. S. Kiiko,[2] and A. L. Ivanovskii[1, 3]

The methodological aspects of using x-ray photoelectron spectroscopy to study the chemical composition, charge state, and electronic parameters of the surface of a complex oxide ceramic containing sections with different electronic conductivity are discussed for ceramic in the system BeO – TiO$_2$ – C. Questions concerning surface preparation of a ceramic by means of Ar$^+$ ion bombardment and mechanical cleaning with a diamond scraper in vacuum are examined.

Key words: BeO – TiO$_2$ – C ceramic, surface, x-ray photoelectron spectroscopy.

Oxide ceramics comprise a wide class of functional materials (refractory, durable, etc.) with a wide spectrum of practical applications. The complex chemical composition and macro- and microstructures, the presence of extended interfaces and intergrain interactions, as well as a number of other factors give rise to substantial difficulties which arise with the use of many conventional physical-chemical methods of constructing a detailed description the structure and properties of these materials. The study of the surface these materials, whose properties strongly influence the service characteristics of specific ceramic composite materials, is also problematic.

An effective method of studying the surface properties of ceramic materials is x-ray photoelectron spectroscopy (XPES).

In the present article a number of methodological aspects of using XPES to study the chemical composition, charge state, and electronic parameters of the surface of oxide ceramic containing sections with different electron conductivity are discussed for ceramics in the system BeO – TiO$_2$ – C. Questions concerning the surface preparation of the ceramic by means of Ar$^+$ ion bombardment and mechanical cleaning with a diamond scraper in vacuum are examined.

We note that a ceramic based on beryllium oxide BO is applicable, for example, as a refractory in special metallurgy, construction materials in electronic technology, materials of fuel elements in nuclear reactors, neutron reflectors, neutron filters, and so on [1 – 5]. Attempts are being made to optimize further the functional characteristics of beryllium-oxide ceramic by modifying it with various additives (for example, titanium dioxide TiO$_2$ and carbon [6, 7]) which are capable of creating different surface microstructures on the boundaries of the crystallites of BeO ceramic [4].

EXPERIMENTAL PROCEDURE

The technology of [6] was used to prepare BeO – TiO$_2$ – C ceramic samples. Chemically pure beryllium oxide and ultrapure titanium dioxide were used as the initial reagents. A mix of BeO with 30%[4] TiO$_2$ added was prepared. The BeO powder was calcined at 1470 K to impart to the powder stable physical-chemical properties. The TiO$_2$ powder was pre-heat-treated at 1070 K. The articles were formed by slip casting using an organic binder. The mix was prepared by wet mixing of the initial oxides in a ball mill for 4 h. The slip, based on a wax-paraffin binder, was prepared in a heated mill at 348 – 358 K. The amount of the organic binder in the slip was 10 – 13%. The organic binder was burned out of the article at 1470 K in 4 h. Sintering was performed in a preparatory furnace with graphite heaters in a carbon monoxide atmosphere (in graphite crucibles and graphite fill, where the CO pressure was varied in the range $1 \times 10^{-2} – 5 \times 10^{-2}$ mm Hg) at maximum temperature near

---

[1] Institute of Solid-State Chemistry of the Urals Branch of the Russian Academy of Sciences, Ekaterinburg, Russia.
[2] Ural State Technical University – Ural Polytechnic University, Ekaterinburg, Russia.
[3] E-mail: ivanovskii@ihim.uran.ru.

---

[2] Here and below — content by weight.

1810 K). The experimental sample (dark with a grey tinge) was prepared in the form of a plate $10 \times 10 \times 2$ mm.

X-ray phase analysis of the ceramic was performed on a STADI-P autodiffractometer, using a CuK$_\alpha$ x-ray source, in the range of angles 2θ from 2 to 100° with step 0.02°. The electronic microscopy of the surface of the ceramic with EDX analysis was performed on a JOEL JSM 6390LA+JED-2300 facility.

XPES measurements of the ceramic were performed on the ESCALAB MK II electronic spectrometer using non-monochromatic MgK$_\alpha$ radiation $h\nu$ = 1253.6 eV. The transmission energy of the analyzer was 20 eV and the scanning step 0.1 eV; the energy resolution of the spectrometer was evaluated according to the width of the Ag3d line at half-height 0.85 eV; calibration of the energy scale was performed according to the C1s line from the surface hydrocarbons (284.5 eV). During the measurements the vacuum was kept at the level 10^{-8} Pa. It is well known that the XPES method analyzes the surface layer of the sample to depth ~ 5 nm, so that to study the "volume" characteristics of ceramic it is important to choose a method for removing surface contaminants from the surface of the sintered sample. Two methods were used in this work: atomization of the surface layers by a beam of argon ions (E = 5 keV, I = 20 µA) and mechanical cleaning of the surface with a diamond scrubber in the vacuum chamber of an electron spectrometer.

RESULTS AND DISCUSSION

According to the XPA data the base of the experimental ceramic BeO – TiO$_2$ – C consists of crystalline oxides BeO and TiO$_2$; in addition, weak additional diffraction peaks (1 – 2% arb. units) belonging to unidentified phases are observed. The content of the phase TiO$_2$ in the sample was about 19%, which corresponds to the formula BeO – 0.08TiO$_2$ – C.

Figure 1 contains images of a ceramic surface which were obtained with a scanning electron microscope. It can be concluded that the ceramic BeO – TiO$_2$ – C is a mechanical mixture of oxides, weakly chemically interacting with one another. The distribution of the TiO$_2$ crystallites in BeO is inhomogeneous; inclusions of regions of grouped TiO$_2$ microcrystals with average size 30 – 70 µm are encountered. Microanalysis of the lateral distribution of the elements over the surface of the ceramic does not show the presence of titanium carbides (or oxycarbides) in the form of free crystallites or layers on the surface of TiO$_2$. A thin layer of carbon, probably in a free state, is present on the boundaries of TiO$_2$ and BeO crystallites (Fig. 1b), but it is difficult to identify its chemical form precisely by the EDX method. To analyze the chemical state of carbon, titanium, and beryllium on the boundaries of the microcrystals of the ceramic requires a special surface-sensitive method, for which x-ray photoelectron spectroscopy was used.
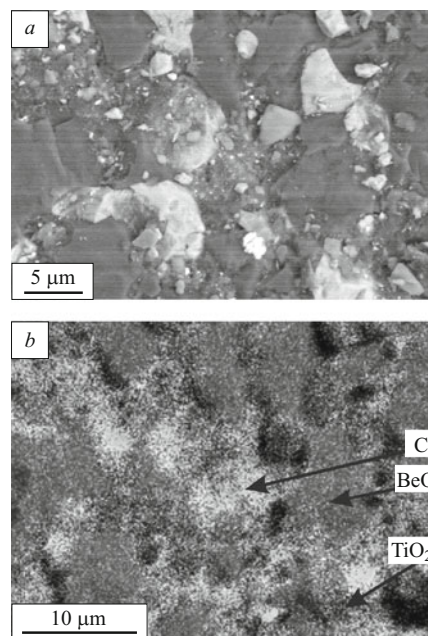

Fig. 1. Image of the surface of the ceramic BeO – TiO$_2$ – C in reflected electrons (*a*) and combined image of the surface in characteristic radiations CK$_\alpha$, OK$_\alpha$, and TiK$_\alpha$ (*b*).

Figure 2 displays panoramic XPES spectra of the surface of a BeO – TiO$_2$ – C ceramic for four variants of its preparation: for the initial surface of the ceramic after sintering (*a*); surface after mechanical cleaning with a scrubber in vacuum (*b*); after ionic sputtering of the surface layers by a Ar$^+$ beam (*c*); and, after repeated mechanical scrubbing in a vacuum (*d*).

The lines of carbon and oxygen from surface contaminants dominate the panoramic spectrum of the surface of the initial sample; peaks due to Ti, Be, silicon, nitrogen, and calcium are also present. The latter three elements are, together with C and O, constituents of the surface contaminants. The strong contamination of the surface of the initial samples makes it necessary to prepare the surface by special methods before measurements are performed. It is extremely difficult to obtain a chip of the beryllium ceramic in the vacuum chamber of the XPES spectrometer, so that alternative methods were used — mechanical cleaning in vacuum and ionic atomization of the surface layers. After the surface is mechanically cleaned with a scrubber in vacuum the silicon, nitrogen, and calcium bands in the panoramic spectrum practically vanish, the intensity of the carbon lines weakens, and the peaks from the electronic states of titanium and beryllium increase (see Fig. 2b).

Even though the band Be1s of the states in the XPES spectrum is relatively weak (because of the small photoionization cross section), the conversion of the intensities of the bands Be1s, Ti2p, O1s, and C1s into atomic concentrations shows that the BeO phase dominates on the surface of the ceramic. Quantitative XPES evaluations of the gross composition of the ceramic in units reduced to the beryllium content give the conventional formula BeO · 0.09TiO$_2$ · xC, which
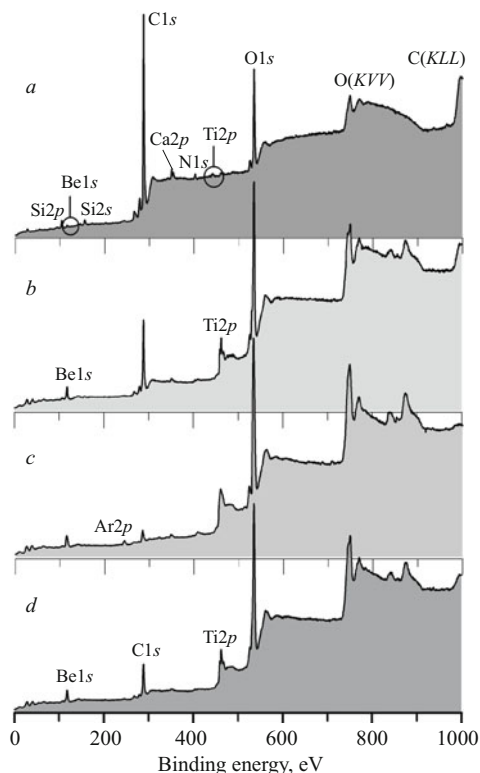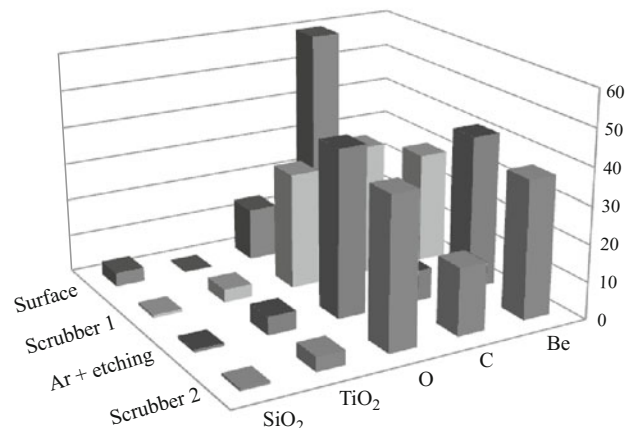
Fig. 2. Panoramic XPES spectra of the surface of BeO – TiO$_2$ – C ceramic: *a*) initial sample; *b*) mechanical working of the surface using a diamond scrubber; *c*) ionic bombardment; *d*) repeated mechanical working.

Fig. 3. Elemental surface composition of the ceramic BeO – TiO$_2$ – C according to XPES as a function of the surface cleaning method.

agrees reasonably well with the XPA data. Here we do not distinguish titanium bound with oxygen in TiO$_2$ and titanium that could be present in other forms in the ceramic, for example, as the carbide TiC owing to the interaction of TiO$_2$ and C on sintering in vacuum.

Next, the surface of the beryllium ceramic was cleaned by means of bombardment with 5-keV Ar$^+$ ions in 10 min. In this case substantial changes occurred in the XPES spectrum (see Fig. 2*c*). In the first place, the intensity of the C1*s* band decreased substantially and the Ar2*p* lines of argon implanted in the surface layer appeared. In the second place, the spectrum of Ti2*p* grew and became transformed. The XPES evaluations of the composition show that the oxygen content in the surface layers of the ceramic drops sharply after ionic cleaning, which affects the degree of oxidation of the metals, first and foremost, titanium. Repeated mechanical cleaning of the surface of the ceramic with a scrubber in vacuum restores the composition of the surface of the ceramic — to the state of the surface before ionic bombardment — with a somewhat lower content of carbon (see Fig. 2*d*).

The surface composition of the ceramic BeO – TiO$_2$ – C at different stages of surface working is shown in Fig. 3, which displays in the form of histograms the atomic concentrations of the components. We call attention to the histogram of the surface of the ceramic after the final mechanical cleaning. It is evident that BeO forms the base of the ce-

ramic. Approximately 9% of the bulk consists of TiO$_2$; in addition, the ceramic contains carbon, whose content is much higher than that of titanium. If this fact could be explained for the initial sample by surface contaminants, then after ionic cleaning and mechanical treatment this result points to the presence of carbon in the ceramic either in the form of an independent phase (soot, graphite, and so on) or in the form of titanium carbide (oxycarbide) on the surface to TiO$_2$ crystallites.

Using the results of the XPES studies, we shall now consider the question of the presence of, besides TiO$_2$, cubic carbide or oxycarbide TiO$_x$C$_y$ in the experimental ceramic. The lowest oxides of Ti can also be present on the surface of TiO$_2$ particles. These forms are not recorded by the XPA method but they exist on the TiO$_2$ surface as a result of the possible reduction of the dioxide in vacuum in the presence of carbon; this should be manifested in the photoelectronic spectra Ti2*p* and C1*s*.

The 1*s* spectra of beryllium are displayed in Fig. 4. For convenience the spectra are presented neglecting the charging of the surface, which is ~ 4.2 eV. Sample charging occurs when the surface of the ceramic is irradiated by an x-ray beam and photoelectrons are emitted from the surface. The magnitude of the charging of the sample depends on the dielectric properties of the material, the dimensions of the sample, the adherence to the conducting substrate, the intensity of the x-ray radiation, and so on. In the case at hand, since BeO is an insulator, the charging of the sample is substantial. But the experimental sample is not simply a BeO ceramic; it contains titanium dioxide, carbon, and possibly titanium carbide. The last two components of the ceramic are conductors and can lower the dielectric characteristics of the sample and, correspondingly, the magnitude of the energy shift of the XPRS spectra.

The presence of charging of the experimental ceramic sample introduces definite difficulties in the interpretation of its XPES spectrum. Complex analysis of the spectra Be1*s*,
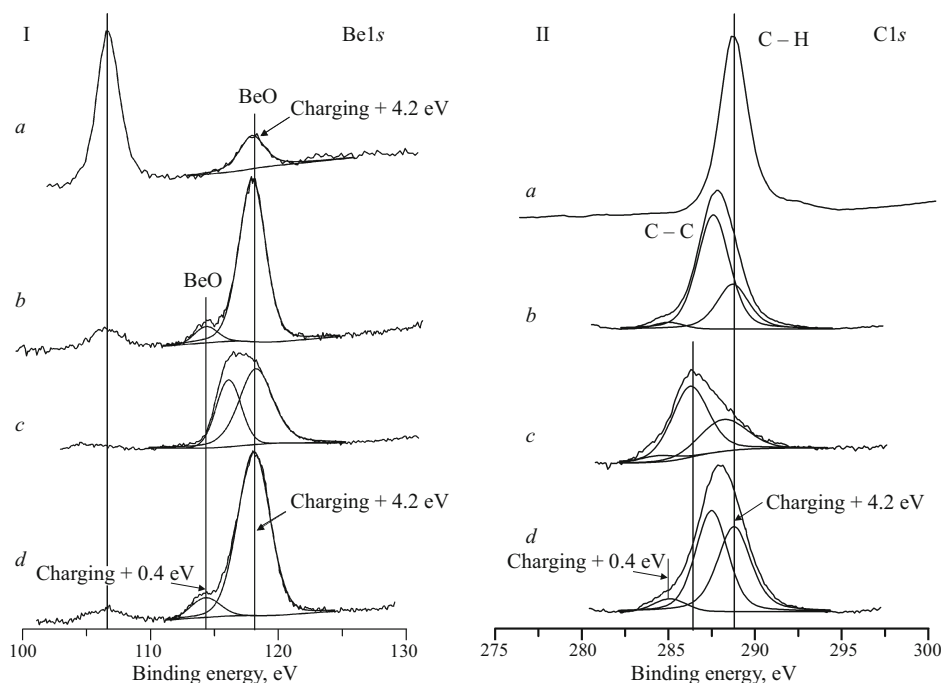
Fig. 4. XPES spectra Be1*s* (I) and C1*s* (II) of the ceramic BeO – TiO$_2$ – C: *a*) initial surface; *b*) after mechanical cleaning; *c*) after Ar$^+$ bombardment; *d*) after a second mechanical cleaning with a diamond scrubber.

C1*s*, O1*s*, and Ti2*p* showed a quite rare situation — nonuniform charging of the surface of the ceramic during XPES analysis. As a result, several bands are present in all photoelectron spectra; but these bands are shifted along the energy scale by a different amount ΔE. The bands correspond to one chemical form of the elements being studied. If this phenomenon is neglected, then the observed lines can be ascribed to different chemical states and it could be incorrectly concluded that a particular compound is present in the ceramic.

On the initial ceramic surface the 118.2 eV line of the Be1*s* states (taking account of the charging 114.0 eV) reflects the chemical form of the beryllium in BeO [8]. Aside from the beryllium band the spectrum contains the intense band of silicon Si2*p* from the surface contaminants (see Fig. 4). This band remains after the surface is worked with a scrubber and ion beam, and it becomes weaker by an order of magnitude. After the mechanical cleaning of the surface with a scrubber in vacuum, an additional component appears in the Be1*s* spectrum on the low binding energy side (shifted by 3.8 eV). This line also corresponds to BeO, but entering into the composition of the fragments of the ceramic with higher conduction properties, where charging is only 0.4 eV.

In the case of ionic bombardment of the ceramic surface by an Ar$^+$ ion beam ($E = 6$ keV) the Be1*s* spectrum broadens because of the appearance of an additional component on the low binding energy side. The new line, shifted by 2.3 eV, is either related with BeO on the sections of the surface with a different conductivity induced by the ion beam or it corresponds to reduced forms of beryllium [8]. Repeated mechanical cleaning of the surface of the ceramic returns the Be1*s* spectrum to the form observed after the first working of the surface by means of a diamond scrubber (see Fig. 4).

Figure 4 also shows the C1*s* spectra of the initial surface of the ceramic and after two forms of working — mechanical cleaning and ion bombardment. Carbon surface contaminations are the dominant forms of carbon on the surface. If charging of the sample (4.2 eV) is taken into account, then the C1*s* band correlates well with the position 284.5 eV corresponding to the chemical bond of carbon C – H. After chemical cleaning the total content of carbon on the surface decreases by a factor 2.5 and the spectrum C1*s* broadens, probably because of a component from elemental carbon which is a constituent of the ceramic. The spectrum C1*s* has one other peak at low binding energies, which is due to carbon atoms on "conducting" ceramic particles. It is shifted relative to the main component C – H by ~ 3.8 eV — by analogy to the low-energy line in the spectrum Be1*s*. After Ar$^+$ ionic cleaning the carbon content on the surface decreases considerably, and the C1*s* spectrum becomes even more "diffuse" because of the differently charged sections of the surface. Repeated mechanical working returns the C1*s* spectrum to the form which it possessed before Ar$^+$ bombardment, and the total intensity of the line decreases somewhat due to the C – C states. The main result following from the analysis of the C1*s* of carbon is that the band from TiC near 281.6 eV is absent [8].

Thus, after the surface of the ceramic is cleaned mechanically two components, shifted relative to one another by ~ 3.8 eV, are observed in the spectra Be1*s* and C1*s*. These components correspond to the same chemical forms of beryllium and carbon but the corresponding elements are found on different sections of the surface with individual charging: some forms of Be and C belong to particles with good conductivity and others belong to sections with high dielectric
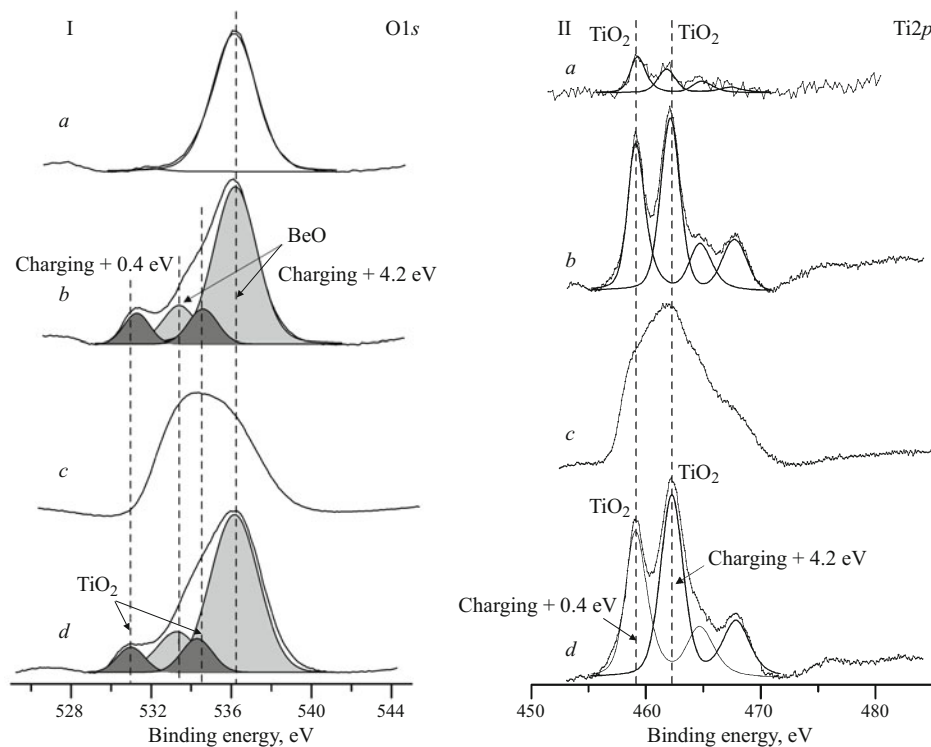
Fig. 5. XPES spectra of O1s (I) and Ti2p (II) of the ceramic BeO – TiO$_2$ – C: *a*) initial surface; *b*) after mechanical cleaning; *c*) after Ar$^+$ bombardment; *d*) after repeat mechanical cleaning of the surface by means of a diamond scrubber.

characteristics. We shall examine from this standpoint the spectra of O1s oxygen and Ti2p titanium.

Figure 5 shows the O1s spectra. As is well known, the O1s binding energy for the oxides BeO and TiO$_2$ are 531.6 eV and 530.0 eV [8], respectively. The single wide band near 536 eV represents the O1s spectrum on the surface of the experimental ceramic. Taking account of the charging of the sample (+ 4.2 eV) this line corresponds to the states of the oxide BeO and oxygen which is a constituent of the surface contaminants: hydrocarbons, sorbed OH$^-$ groups, SiO$_2$, and so on. The titanium content on the surface is low (see Fig. 3), so that the contribution of TiO$_2$ to the O1s band of oxygen is negligible.

After mechanical cleaning, additional peaks shifted to low binding energies, appear in the O1s spectrum. It is difficult to decompose the spectrum obtained into individual components. Based on the assumption that two types of sections with charging + 4.2 and + 0.4 eV are present on the surface and knowing the chemical shift of the level O1s in BeO relative to TiO$_2$, the oxygen spectrum was decomposed into four peaks: one pair of bands corresponds to the states of oxygen in TiO$_2$ and the other pair corresponds to oxygen in BeO. The spectrum of the second band agrees in form with the spectrum of Be1s in Fig. 4 and reflects the state of oxygen in BeO in two differently charged fragments of the ceramic in the proportion ~ 6 : 1 in favor of the main dielectric part. In the case of TiO$_2$ of the component of the spectrum O1s, conversely, an equal proportion is observed between the maxima of the "dielectric" and "conducting" particles of the chemical compound corresponding to titanium dioxide. It is

found that on sections of the ceramic with high conductivity the titanium content is much higher than that of beryllium.

Ionic bombardment greatly broadens the spectrum O1s, which makes it impossible to interpret the chemical states of oxygen on the surface of the ceramic correctly. After repeat mechanical cleaning in vacuum the O1s spectrum is identical to the spectrum after the first mechanical working. The reproducibility of the results indicates that this method of surface preparation of BeO – TiO$_2$ – C ceramic prior to XPES analysis is preferable.

Figure 5 also shows the XPES spectra of the 2p states of titanium. The form of these spectra can easily lead to incorrect conclusions concerning the chemical bond of titanium in the BeO – TiO$_2$ – C ceramic. Indeed, the band 2$p_{3/2}$ + 2$p_{1/2}$ for high binding energies is uniquely related with the dioxide TiO$_2$: taking account of the shrinkage of the sample the binding energy E_b of the level Ti2$p_{3/2}$ of this doublet is 458.0 eV, which corresponds to the degree of oxidation of titanium Ti^{4+} [8]. It is logical to assume that the second doublet for lower values of E_b must correspond to a lower degree of oxidation of titanium. For energy splitting ÄE between the doublets ~ 3 eV the maximum of the level Ti2$p_{3/2}$ of the second doublet has a binding energy 545.0 eV, which agrees well with the analogous quantities for TiC$_x$ or TiC$_x$O$_y$ [8].

However, a more detailed analysis leads to different conclusions. In the first place, the form of the spectrum Ti2p of titanium carbide differs strongly from that of TiO$_2$, while the two doublets obtained have the same decomposition parameters, corresponding to titanium dioxide. In the second place the analogous energy shift (ΔE = 3.8 eV) is observed in all the experimental spectra (Be1s, C1s, O1s, Ti2p), and there-
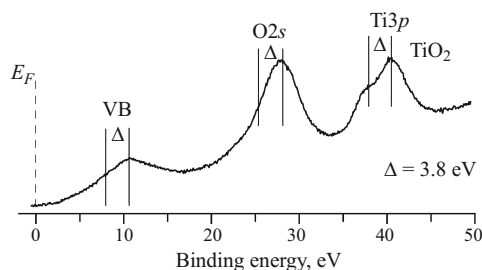
Fig. 6. XPES spectrum of the valence band of the surface of the ceramic BeO – TiO$_2$ – C after mechanical cleaning with a diamond scrubber (charging of the sample was neglected).

fore it is determined not by a different chemical (valence) form of titanium (beryllium and so on) but rather the charging of the sample under the x-ray beam. Finally, the intensities of the two Ti2p doublets (see Fig. 5) are close to one another. This agrees with the proportional ratio of the two oxygen lines which are associated with TiO$_2$.

Thus, two components are present in approximately equal proportion in the Ti2p spectra of titanium. These components correspond to the same chemical compound of titanium — TiO$_2$, but they characterize the structural fragments of the ceramic BeO – TiO$_2$ – C with different conducting properties.

After ionic bombardment of the surface the Ti2p spectrum of titanium becomes diffuse and, strictly speaking, cannot be uniquely decomposed into individual chemical compounds of titanium (see Fig. 5). It is known that under ion bombardment the surface layers of TiO$_2$ are partially reduced to Ti$_2$O$_3$ and Ti$_3$O$_5$; in the Ti2p spectrum they correspond to the bands on the low binding energy side of the doublet 2p from TiO$_2$ [8]. In addition, the TiO$_2$ particles with a reduced surface possess the best conductivity and the 2$p_{3/2}$ and 2$p_{1/2}$ bands correspondingly are also shifted in the direction of low values of E_b as a result of a decrease of the charging of the particles.

Thus, the ionic Ar$^+$ cleaning of the surface of a ceramic has a negative effect on the spectra of the Ti2p states (and also Be1s, C1s, O1s), introducing changes in the surface composition and in the chemical form of the atoms of the components. It is obvious that this method of preparing the surface of a ceramic is ineffective. Conversely, with mechanical cleaning of the surface with a scrubber in vacuum it is possible to eliminate contaminants from the surface and make the surface composition approach the parameters in the interior volume of the ceramic.

In conclusion, we present the spectrum of the valence band (VB) of the experimental sample of the ceramic BeO – TiO$_2$ – C after chemical cleaning with a scrubber in vacuum (Fig. 6). The total spectrum is a superposition of two identical spectra VB shifted with respect to one another by the amount of the charging of the two fractions of the ceramic ($\Delta E = 3.8$ eV). The result proves once again that in the experimental ceramic nonuniform charging of the sections of

the surface and not chemical different compounds of the elements occurs.

CONCLUSIONS

A number of methodological aspects of using x-ray photoelectron spectroscopy to study the chemical composition, charge state, and electronic parameters of the surface of a complex oxide ceramic BeO – TiO$_2$ – C were discussed.

Analysis of the photoelectron spectra of Be1s, C1s, O1s, and Ti2p revealed a quite rare situation: nonuniform charging of the surface of the ceramic with several bands shifted on the energy scale by a different amount ΔE present in all photoelectron spectra. The bands correspond to a single chemical formula of the elements considered. The main fraction of the beryllium ceramic manifests pronounced dielectric properties. However, there exists a small component which manifests good electric conductivity. According to XPES, approximately half the titanium atoms in the compound TiO$_2$ are in this "conducting phase."

Comparing the two methods of preparing the surface of a ceramic for XPES analysis — ionic atomization of the surface with a Ar$^+$ beam and mechanical cleaning of the surface with a diamond scrubber in vacuum — it is obvious that the latter has obvious advantages. Under ionic bombardment of the surface of the ceramic artificial reduction of the titanium oxide to lower forms and a substantial change of the gross-composition of the surface occur.

REFERENCES

1. R. A. Belyaev, *Beryllium Oxide* [in Russian], Atomizdat, Moscow (1980).
2. V. S. Kiiko, "Anomalous properties of BeO and ceramic based on it," *Neorgan. Mater.*, **37**(11), 1397 – 1401 (2001).
3. A. L. Ivanovskii, Yu. N. Makurin, V. S. Kiiko, et al., "Electronic structure and properties of beryllium oxide," *Neorgan. Mater.*, **45**(3), 223 – 234 (2009).
4. V. S. Kiiko, Yu. N. Makurin, and A. L. Ivanovskii, *Ceramics Based on Beryllium Oxide: Production, Physical-Chemical Properties, and Applications* [in Russian], Izd. UrO RAN, Ekaterinburg (2006).
5. G. P. Akishin, S. K. Trunaev, V. Ya. Vaispapip, et al., "Thermal conductivity of beryllium-oxide ceramic," *Novye Ogneupory*, No. 12, 43 – 47 (2009).
6. V. S. Kiiko, "Effect of titanium dioxide additions on the physical-chemical and luminescence properties of beryllium ceramic," *Neorgan. Mater.*, **30**(5), 688 – 693 (1994).
7. V. S. Kiiko, M. A. Gorbunova, Yu. N. Makurin, et al., "Microstructure and electric conductivity of composite (BeO + TiO$_2$) ceramic," *Novye ogneupory*, No. 11, 68 – 74 (2007).
8. J. F. Moulder, F. W. Stickle, P. E. Sobol, and K. D. Bomben, in: J. Chastain and R. C. King (eds.), *Handbook of X-Ray Photoelectron Spectroscopy*, Physical Electronics, Inc., New York (1995).